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(54) METHOD FOR REDUCING HARMFUL EMISSIONS FROM A DIESEL ENGINE EQUIPPED WITH A PARTICULATE TRAP

METHODE ZUR HERABSETZUNG DES SCHADSTOFFAUSSTOSSES AUS EINEM MIT EINER PARTIKELFALLE VERSEHENEM DIESELMOTOR

PROCEDE DE REDUCTION DES EMISSIONS NOCIVES D'UN MOTEUR DIESEL EQUIPE D'UN PIEGE A PARTICULES

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(56) References cited:
US-A- 2 086 775
US-A- 2 151 432
US-A- 4 568 357
US-A- 4 603 215
US-A- 5 034 020

- **2-5 November 1987, McCABE et al., "Oxidation of Diesel Particulates by Catalyzed Wall-Flow Monolith Filters. 2. Regeneration Characteristics of Platinum, Lithium, and Platinum Lithium Catalyzed Filters"; Society of Automobile Engineers, Paper No. 872137, (All).**
- **19-22 October 1992, BECKMANN et al., "A New Generation of Diesel Oxidation Catalysts", Society of Automobile Engineers, Paper No. 933330 (All).**
- **19-22 October 1992, KRUTZSCH et al., "Effect of Sodium and Lithium Based Fuel Additives on the Regeneration Efficiency of Diesel Particulate Filters", Society of Automotive Engineers, Paper No. 922188, (All).**
- **1981, MURPHY et al., "Assessment of Diesel Particulate Control-Direct and Catalytic Oxidation", Society of Automotive Engineers, Paper No. 810112, (All).**
- **23-25 September 1985, SNIDER et al., "Control of Diesel Engine Exhaust Emissions in Underground Mining", 2nd. U,S, Mine Ventilation Symposium, Reno Nevada, pages 637-642.**

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The file contains technical information submitted after the application was filed and not included in this specification

Description

Related Applications

[0001] This application is a continuation-in-part of copending and commonly assigned WO-A-9 312 207, entitled "Method for Reducing the Particulate Emissions from a Diesel Engine", filed in the names of Peter-Hoblyn, Valentine, Epperly, and Sprague on December 16, 1991, which in turn is a continuation-in-part of copending and commonly assigned U.S. A-5 501 714 and US-A-5 266 083 entitled "Method for Reducing Emissions From or Increasing the Utilizable Energy of Fuel for Powering Internal Combustion Engines", filed in the names of Epperly, Sprague, Kelso, and Bowers, on November 12, 1991, which in turn is a continuation of WO-A-9-007 561.

Technical Field

[0002] Diesel engines are typically equipped with particulate traps, mounted in the exhaust stream, to "trap" or collect particulates in the exhaust to prevent their emission to the atmosphere.

[0003] Diesel engines running without particulate traps emit unburned hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_x), and particulates, all of which are subject to current or proposed regulation. The problems of controlling these pollutants are compounded because there is a trade-off between particulates and nitrogen oxides -- when the combustion conditions are modified to favor low nitrogen oxides emissions, particulates are increased. The problems are further compounded when particulate traps are employed to reduce the severity of the particulate emissions because particulate traps tend to increase the production of carbon monoxide. And, even with a trap, unburned hydrocarbons remain a problem.

[0004] It now appears that a combination of techniques, including diesel traps, will be required to meet realistic clean air goals. This manner of reducing particulates will be necessary because the techniques available for NO_x reduction, such as timing changes and exhaust gas recirculation, require a trade-off with particulates. The achievement of lower emissions of NO_x, unburned hydrocarbons, and carbon monoxide, while controlling particulates over reasonable periods of time, continues to present a technical challenge.

Background Art

[0005] Diesel particulates, their effect and control, are at the center of much concern and controversy. Their chemistry and environmental impact present complex issues. Generally, the diesel particulate matter is principally solid particles of carbon and metal compounds with adsorbed hydrocarbons, sulfates and aqueous species. Among the adsorbed species are aldehydes and polycyclic aromatic hydrocarbons (also called PAH's). Some of these organics have been reported to be potential carcinogens or mutagens. Unburned hydrocarbons are related to the characteristic diesel odor and include aldehydes such as formaldehyde and acrolein. The aldehydes, like carbon monoxide, are products of incomplete combustion.

[0006] It is not just these organics which are of concern. In one study, diesel particulates were tested along side TiO_2 and carbon without any adsorbed hydrocarbons. (U. Heinrich, *et al*, "Tierexperimentelle Inhalationsstudien Zur Frage der Tumorinduzierenden Wirkung von Dieselmotorabgasen und zwei Teststauben", *Oklolgische Forschung BMFT/GSF*, Munich, 1992) The reporters determined that all species tested showed carcinogenic tendency. Until further work clarifies this matter, it would be prudent to look for systems which could control particulates of any composition.

[0007] Unfortunately, increasing the recovery of particulates simply by modifying trap design or size would increase the rate of back pressure buildup within the trap. Moreover, control of the various pollutants seems to be interrelated, with reduction of one sometimes increasing levels of another. By modifying combustion to achieve more complete oxidation, decreases can be achieved for pollutants resulting from incomplete combustion, but NO_x is typically increased under these conditions.

[0008] NO_x, principally NO and NO_2, contributes to smog, ground level ozone formation and acid rain. NO is produced in large quantities at the high combustion temperatures associated with diesel engines. The NO_2 is formed principally by the post oxidation of NO in the diesel exhaust stream. Several attempts have been made to reduce NO_x, such as by retarding engine timing, exhaust gas recirculation, and the like; however, with current technology, there is a trade-off between NO_x and particulates. When NO_x is reduced, particulate emissions increase. And, as noted, conditions favoring low emissions of NO_x often favor production of increased levels of CO and HC.

[0009] It is clear that diesel traps (either catalyzed or uncatalyzed) will be required in order to control particulates, especially where efforts are made to control NO_x. However, the use of uncatalyzed traps increases carbon monoxide and the use of catalyzed traps has other disadvantages -- notably increases in the discharge of SO_3 and thus total particulates and other problems.

[0010] The use of Diesel traps and the need to improve them has resulted in a great deal of research and a great number of patents and technical publications. The traps are typically constructed of metal or ceramic and are capable of collecting the particulates from the exhaust and with-standing the heat produced by oxidation of carbonaceous deposits which must be burned off at regular intervals.

[0011] This burning off, or regeneration, could occur by itself if the operating temperature of the trap were sufficiently high. However, in the typical situation, the exhaust temperature is not constantly high enough, and secondary measures such as electrically heating to raise the trap temperature or using a catalyst to reduce the combustion temperature of particulates, have not been fully successful.

[0012] The use of trap heaters creates an intense load on batteries, especially because they are most needed at lower power settings where the electrical output is also low. The use of catalysts has taken many forms, but none have been found to be fully satisfactory. While catalysts can be very effective in reducing carbon monoxide and unburned hydrocarbons, they can be too easily fouled, have associated health risks, and/or catalyze the oxidation of SO_2 to SO_3 (which then combines with water and increases the weight of particulates), or have two more of these shortcomings.

[0013] In a recent assessment of this technology, R. Beckman *et al* assert that the technical challenge is to find a catalyst which selectively catalyzes the oxidation of carbonaceous components at low exhaust temperatures typical of diesels operating at partial load, and does not oxidize sulfur dioxide or nitrogen oxide at high load temperatures. ("A New Generation of Diesel Oxidation Catalysts", *Society of Automotive Engineers (SAE) Paper No. 922330, 1992)* They described tests studying the aging of platinum-catalyzed cordierite honeycomb traps, and concluded, *inter alia*, that the aging was related to adsorption of sulfur and that this depended on both the sulfur content of the fuel and the phosphorous content of the lubricating oil. With control of both of these, aging could be slowed. However, sulfur will remain in diesel fuels, even with planned reduction to 0.05%, and there will remain a need for a means to maintain the activity of catalysts for reducing emissions of carbon monoxide, unburned hydrocarbons, and reducing the ignition temperature of loaded traps.

[0014] In "Control of Diesel Engine Exhaust Emissions in Underground Mining", 2nd U. S. Mine Ventilation Symposium, Reno, Nevada, Sept. 23-25, 1985, at page 637, S. Snider and J. J. Stekar report that precious metal catalysts in a catalytic trap oxidizer and a "catalyzed Corning trap" were effective in the capture of particulate matter, but both systems increased the conversion of SO_2 to SO_3. The increase in the rate of oxidation of the benign, gaseous dioxide form to the trioxide form results in the adsorption of greater amounts of acid sulfates and associated water onto the particulates discharged. Thus, the weight of the particulates is increased, and the difficulty in reaching regulatory compliance is increased.

[0015] The Snider *et al* report also discussed several other approaches, including the use of a fuel additive containing 80 ppm manganese and 20 ppm copper to reduce the regeneration temperature of the trap. While this was effective in reducing the particulate ignition temperature, these "base metal" catalysts were potentially problematic. Moreover, no measurable reductions in carbon monoxide, unburned hydrocarbons or NO_x were noted.

[0016] In "Assessment of Diesel Particulate Control - Direct and Catalytic Oxidation", *Society of Automotive Engineers (SAE) Paper No. 81 0112*, 1981, Murphy, Hillenbrand, Trayser, and Wasser have reported that the addition of catalyst metal to trapped particulates can decrease particulate ignition temperatures. The catalysts were metal chlorides, including platinum chlorides. The use of halogens in platinum compounds, however, can lead to vaporization of the catalyst metal compound. Moreover, the above Snider *et al* article indicates that precious metal catalysts could be expected to increase the oxidation of SO_2 to SO_3.

[0017] In a 1987 report, R. W. McCabe and R. M. Sinkevitch summarized their studies of diesel traps catalyzed with platinum and lithium, both individually and in combination (Oxidation of Diesel Particulates by Catalyzed Wall-Flow Monolith Filters. 2. Regeneration Characteristics of Platinum, Lithium, and Platinum-Lithium Catalyzed Filters; *SAE Technical Paper Series-872137*). They noted that carbon monoxide conversion to the dioxide was negligible over the lithium filter, good for platinum, but good only initially for the combined catalyst. They further noted that platinum undergoes a reversible inhibition due to the presence of SO_2, but in the presence of the lithium catalyst there is apparently a wetting of the platinum crystallites by Li_2O_2.

From this work, it can be seen that platinum and lithium on their own help burn out at low temperature, but not necessarily low enough to make supplemental heat unnecessary.

[0018] In a more recent report, B. Krutzsch and G. Wenninger discussed their investigation of sodium and lithium-based fuel additives (Effect of Sodium- and Lithium-Based Fuel Additives on the Regeneration Efficiency of Diesel Particulate Filters, *SAE Technical Paper Series 922188*, 1992). They noted that the predominantly used diesel additives were based on transition metals such as iron, copper, and manganese. They were interested in the sodium and lithium catalysts, however, because of the health concerns with the others. Moreover, the transition metals were seen to form oxides which foul the traps and cannot be easily removed. They found that the sodium and lithium additives did permit regeneration at temperatures low enough to possibly eliminate the need for supplementary heat, and did, therefore, have some promise in improving trap operation as was achieved previously with the transition metal catalysts. However, they also pointed out that there was no effect on the gaseous components, thus both carbon monoxide and unburned

hydrocarbon levels remained higher than would be desired.

[0019] There is a present need for an improved means for rendering the exhaust from diesel engines more environmentally benign, and, especially to enable this without requiring engine retrofitting, the use of expensive catalytic units, or creating health concerns either from catalysts employed or the production of harmful by-products such as increased levels of sulfates in the discharged particulates.

Disclosure of Invention

[0020] The present invention relates to a method for improving the operation of a diesel trap, either catalyzed or uncatalyzed, and if catalyzed in any stage of activity. The method comprises the addition of fuel-soluble compositions of platinum group metal to a diesel fuel in an amount of at least 0.05 ppm up to 30 ppm, i.e. in effective amounts such that the exhaust produced by combustion selectively catalyzes the exhaust system, including a diesel trap, effectively to lower the emissions of unburned hydrocarbons and carbon monoxide. By the term "selectively catalyzes" it is meant a catalytic activity is achieved to reduce emissions of carbon monoxide and unburned hydrocarbons as compared to an uncatalyzed trap, but causes less conversion of SO_2 to SO_3 than a trap catalyzed with platinum prior to operation. Furthermore, at least one of a cerium compound, an iron compound and a copper compound is added to the diesel fuel in an amount of from about 5 to about 100 ppm. The invention enables depositing sufficient catalyst in the exhaust system to reduce the regeneration temperature of the trap. In one alternative embodiment platinum and/or sodium or lithium compositions can be injected into the exhaust system to rapidly build up catalyst in the trap.

[0021] The platinum group metal compositions are preferably soluble in the diesel fuel and added in amounts effective to provide concentrations of the metal in the fuel of less than 1 part per million (ppm). The lithium and sodium compositions are preferably used in amounts to provide concentrations of lithium in the fuel of from 1 to 100 ppm, when employed, and sodium at 1 to 30 ppm, when employed. For the purposes of this description, all "parts per million" figures are on a weight to volume basis, *i.e.*, grams/million cubic centimeters (which can also be expressed as milligrams/liter), and percentages are given by weight, unless otherwise indicated.

Description of the Drawings

[0022] The invention will be better understood and its advantages will be more apparent when the following detailed description is read in light of the accompanying drawings, wherein:

Figure 1 is a chart which presents a summary of results from the tests of Comparative Example 1, comparing baseline and final results on unburned hydrocarbon emissions both following a particulate trap and in an exhaust system which bypasses a trap;

Figure 2 is a chart, similar to that of Figure 1, but showing the results for carbon monoxide emissions;

Figure 3 is a chart, similar to that of Figure 1, but summarizing the results for particulate emissions;

Figure 4 is a graph showing the efficiency of hydrocarbon conversion for the present invention as compared to other test systems;

Figure 5 is a graph, similar to that of Figure 4, but showing the selectivity of the invention on sulfur conversion; and

Figure 6 is a graph presenting the data for Figures 4 and 5 to illustrate the tradeoff between sulfur and hydrocarbon conversion.

Detailed Description of the Preferred Embodiment

[0023] In this description, the term "diesel engines" is meant to include those reciprocating engines capable of being run on "diesel fuel", as defined by the American Society of Testing and Management (ASTM) Standard Specification for Fuel Oils (designation D 396-86). More generally, diesel fuel can be fuel oil No. 2 or No. 4 petroleum distillates as well as alternative diesel fuels containing emulsified water or alcohols such as ethanol or methanol, as long as they exhibit volatility and cetane number characteristics effective for the purpose.

[0024] The invention concerns diesel engines equipped with or having associated therewith a diesel engine particulate trap. By this it is meant that a diesel engine particulate trap is disposed such that the exhaust stream from the engine passes therethrough. Generally, a diesel engine particulate trap is disposed on the tailpipe of the vehicle in which the diesel engine is located, downstream from the exhaust manifold.

[0025] Suitable diesel traps are known to the skilled artisan and generally comprise an apparatus designed to trap or collect particulates which are present in the exhaust stream of the diesel engine. Such a trap can be made of any suitable material such as ceramic (for instance, a cordierite ceramic material), glass fiber, or metal. In addition, the trap can be coated with a catalytic material to facilitate regeneration. It is an advantage of the present invention, however, that the traps are selectively catalyzed during operation and are constantly maintaned by the additive.

[0026] Since flow resistance to the exhaust increases in proportion to the efficiency of the diesel trap at collecting particulates, a compromise must be made between trap efficiency and exhaust back pressure. One type of diesel engine particulate trap which is found to be effective at trapping particulates while still providing an acceptable compromise in terms of back pressure created are traps available under the trademarks Dieselfilter or EX 51 100/17 from Corning Glass Corporation of Corning, New York.

[0027] Suitable diesel engine particulate traps typically consist of a gas permeable material, such as a ceramic. The trap is formed such that it has at least two (and generally several) parallel gas channels longitudinally arranged in a honeycomb-type structure extending between what can be referred to as an upstream, or engine-side, face and a downstream, or exhaust-side, face. Each channel is plugged at one of its faces such that alternate faces of adjacent channels are plugged. In this way, exhaust entering the trap through a channel at its unplugged upstream face must pass through a wall into an adjacent channel in order to exit the trap from its unplugged downstream face. Particulates in the exhaust are then trapped or collected on the wall. Such a trap is described, for instance, in U.S. Patent 4,568,357 to Simon.

[0028] The particulate trap used in the method of the present invention can be one which is self-regenerating, that is, trapped particulates are ignited by heat derived from the engine, usually from the hot exhaust gasses themselves. In order to reduce particulate buildup on the trap, it is desired that the particulates are combusted or "burned off" the trap in order to free the surface thereof for further collection of particulates. Under normal conditions, and without the use of a catalyst, temperatures of at least about 600°C are believed to be required to combust the particulates and, thus, regenerate the trap. Since a four-stroke diesel engine produces an exhaust which operates at an average temperature between about 400°C and 500°C, and which only occasionally reaches temperatures in excess of 600°C, the typical exhaust temperature is too low to lead to effective trap regeneration. A two-stroke diesel engine produces an exhaust which is at an even lower temperature, and which rarely exceeds 600°C, making trap regeneration even more reliant on auxiliary heat.

[0029] The fuel additives of the invention improve the operation of a diesel trap, either catalyzed or uncatalyzed, and if catalyzed in any stage of activity. The method comprises the addition of fuel-soluble compounds of a platinum group metal composition to a diesel fuel in an amount of at least 0.05 ppm up to 30 ppm, i.e. in effective amounts such that the exhaust produced by combustion selectively catalyzes the exhaust system, including the diesel trap, effectively to lower the emissions of unburned hydrocarbons and carbon monoxide. Furthermore, at least one of a cerium compound, an iron compound and a copper compound is added is added in an amount of from 5 to 100 ppm. The invention enables depositing sufficient catalyst, which can also comprise sodium or lithium, in the exhaust system to reduce the regeneration temperature of the trap.

[0030] The platinum group metal compositions are preferably soluble in the diesel fuel and added in amounts effective to provide concentrations of the metal in the fuel of less than 1 part per million (ppm). The lithium and sodium compositions, when employed, are preferably used in amounts to provide concentrations of from 1 to 100 ppm metal in the case of lithium, and at 1 to 30 ppm metal in the case of sodium.

[0031] Among the suitable lithium and sodium compositions are the salts of lithium and sodium respectively, with suitable organic compounds such as alcohols or acids, *e.g.*, aliphatic, alicyclic and aromatic alcohols and acids. Exemplary of particular salts are the lithium and sodium salts of tertiary butyl alcohol and mixtures of these. Other lithium and sodium organic salts are available and suitable for use to the extent that they are fuel-soluble and are stable in solution. While not preferred, inorganic salts can also be employed to the extent that they can be efficiently dispersed in the fuel, such as in a stable emulsion or otherwise, and have the desired effect in the exhaust system including the trap. These compositions should be free of the contaminants mentioned below which will affect the performance of the platinum group metal.

[0032] In alternative embodiments the additives can be employed with gasoline fuel in internal combustion engines operating with exhaust catalysts. The useful salts of iron, copper and cerium are employed at suitable levels, i.e., from 5 to 100 ppm and preferably 30 to 60 ppm of the catalyst metal in combination with the platinum group metal composition in diesel fuels or gasoline. In these embodiments the addition of platinum group metal catalysts according to the invention reduces the level of unburned hydrocarbons and carbon monoxides while obtaining the known effects of these other catalyst metals.

[0033] Preferred additives comprise a diesel fuel soluble organometallic platinum group metal coordination composition and a diesel fuel soluble composition of sodium and/or lithium. The additive compositions should be temperature stable, and substantially free of phosphorus, arsenic, antimony, or halides. Advantageously, the additive also has a partition ratio sufficient to maintain significant preferential solubility in the fuel in order to effectively enhance combustion.

[0034] The organic nature of the compositions provides solubility in diesel fuel, thereby facilitating the introduction of the additive into the combustion chamber of a diesel engine. Without such solubility, much of the additive would precipitate in the fuel tank or fuel lines of the diesel engine prior to introduction into its combustion chamber.

[0035] Temperature stability of the additive is very important in practical and operational terms. In a commercial setting, a fuel additive is packaged and then can often sit on a store shelf or in a delivery truck for extended periods of time during which the additive can be exposed to great variations in temperature. If the breakdown temperature of the additive is not sufficiently high (*i.e.*, if the additive is not temperature stable at the temperatures to which it is expected to be exposed), then the packaged additive will quickly break down and become virtually useless.

[0036] Moreover, breakdown of the additive after mixing with the fuel will render the additive insoluble in the fuel, since the solubility is provided by the organic functional groups. Such loss of solubility will cause the additive to precipitate and not reach the combustion chamber, as discussed above. This becomes important when the additive is mixed into the fuel in advance of the fuel being provided to the fuel system of the engine (as opposed to a separate additive reservoir on the vehicle, with mixing occurring immediately prior to combustion), as desired.

[0037] Typically, the breakdown temperature of the additive should be at least about 40°C, preferably at least about 50°C, in order to protect against most temperatures to which it can be expected to be exposed. In some circumstances, it will be necessary that the breakdown temperature be no lower than about 75°C.

[0038] The organic nature of the preferred platinum group metal compositions helps to maintain the composition in solution in an organic solvent which provides a convenient diluent and can have functional properties, thereby preventing "plating out" of the platinum group metal composition in the packaging medium.

[0039] The additive of the present invention should be substantially free from objectionable traces of, or functional groups containing, phosphorus, arsenic, antimony, and, especially, halogens (*i.e.*, they should not contain a substantial amount of such functional groups) which have significant disadvantages like "poisoning" or otherwise reducing the effectiveness of the platinum group metal composition catalyst or the sodium or lithium compositions if employed. Halogens have the additional undesirable effect of rendering a platinum group metal more volatile, leading to reduction of the amount of platinum group metal in the combustion chamber and engine system.

[0040] A substantial amount of such functional groups is considered an amount effective to significantly reduce the effectiveness of the catalyst. Preferably, the purified platinum group metal additive composition contains no more than about 500 ppm (on a weight per weight basis) of phosphorus, arsenic, antimony, or halogens, more preferably no more than about 250 ppm. Most preferably, the additive contains no phosphorus, arsenic, antimony, or halogens.

[0041] Such objectionable functional groups can be minimized in several ways. The platinum group metal composition can be prepared in a process which utilizes precursors or reactant compositions having a minimum of such functional groups; or the additive can be purified after preparation. Many such methods of purification are known to the skilled artisan.

[0042] One preferred method of purifying the platinum group metal additive to remove halogens is a process utilizing silver salts having non-halide anions which are harmless as compared to the halogens being replaced and involves reacting them with the platinum group metal compound, whereby the halogens in the composition are replaced by the anion of the silver salt (which can be any silver salts of carboxylic acids, such as silver benzoate, or silver nitrate) and the resulting composition is free of halogens, plus a silver halide is produced.

[0043] For instance, a slurry or solution in a polar solvent such as acetone or an alcohol and water of silver nitrate or silver benzoate can be prepared and reacted with the platinum group metal composition. The resultant platinum group metal composition is a benzoate or nitrate salt with silver halide also being produced. This process can be expected to reduce the halogen content of a sample by about 50%, and even up to about 90% and higher.

[0044] The relative solubility of the additive in the diesel fuel and water is also important since there is often a substantial amount of water admixed with the fuel. This relative solubility is referred to as the partition ratio and can be expressed as the ratio of the amount in milligrams per liter of composition which is present in the fuel to the amount which is present in the water. This can most easily be determined in a 100 milliliter (ml) sample which is 90% fuel and 10% water. By determining the amount of composition in the fuel and the amount in the water, the partition ratio can be readily determined.

[0045] The preferential solubility of the additive in fuel as compared to water can be critical because if a substantial amount of the additive is dissolved in the water which may be present, the overall effectiveness of the additive can be proportionally reduced. This partition ratio should be at least about 25 and is most preferably greater than about 50.

[0046] In order to reduce the water susceptibility of the platinum group metal composition, it is especially desired that the composition have at least one platinum group metal-to-carbon covalent bond. A platinum group metal-to-oxygen or platinum group metal-to-nitrogen bond can be acceptable, but there must also be at least one metal to carbon bond. Platinum group metals include platinum, palladium, rhodium, ruthenium, osmium, and iridium. Compounds including platinum, palladium, and rhodium, especially compounds of platinum alone or possibly in combination with rhodium compounds are preferred in the practice of this invention since the vapor pressure of these metals is sufficiently high to facilitate the desired reduction of carbon monoxide emissions.

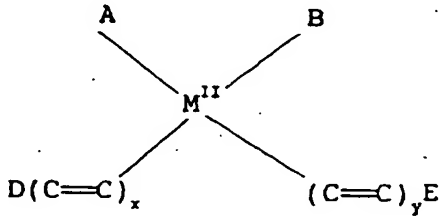
[0047] The preferred class of fuel soluble catalyst compositions include compounds where the platinum group metal exists in oxidation states II and IV. Compounds in the lower (II) state of oxidation are preferred due to their function in generating the catalytic effect. A significant feature of the invention is the use of platinum group metal II coordination compounds having at least one coordination site occupied by a functional group containing an unsaturated carbon-to-carbon bond. Preferably, two or more of the coordination sites will be occupied by such functional groups since the stability and solubility in diesel fuel of compounds having such multiple functional groups are improved. While not wishing to be bound to any particular theory, it is believed that such preferred compounds in the lowest possible oxidation state are the most beneficial for producing the desired catalytic effect.

[0048] Occupation of one of more coordination sites with the following unsaturated functional groups has been found useful:

1. Benzene and analogous aromatic compounds such as anthracene and naphthalene.
2. Cyclic dienes and homologues such as cyclooctadiene, methyl cyclopentadiene, and cyclohexadiene.
3. Olefins such as nonene, dodecene, and polyisobutenes.
4. Acetylenes such as nonyne and dodecyne.

[0049] These unsaturated functional groups, in turn, can be substituted with nonhalogen-substituents such as alkyl, carboxyl, amino, nitro, hydroxyl, and alkoxyl groups. Other coordination sites can be directly occupied by such groups.

[0050] The general formula for the preferred coordination II compounds is:



where M^{II} represent the platinum group metal, with a valence of +2, where A, B, D, and E are groups such as alkoxy, carboxyl, etc. described above, where $(C{=}C)_x$ and $(C{=}C)_y$ represent unsaturated functional groups coordinated with the platinum group metal, and where x and y are any integer, typically 1 to 5.

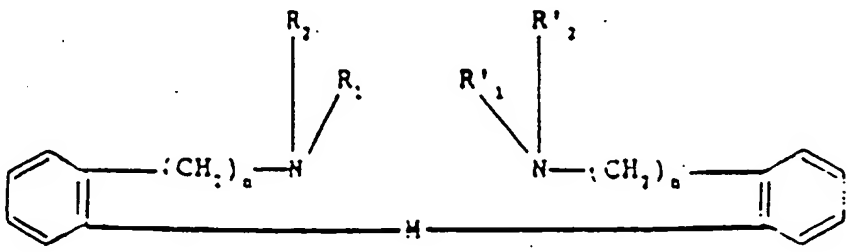
[0051] The most preferred platinum group coordination compounds are those represented by the following formula:

$$XM^{II}R_2$$

wherein X is a cyclooctadienyl ligand, M is a platinum group metal, and R is benzyl, phenyl, or nitrobenzyl.

[0052] Among other platinum group metal compounds, are the following which include at least one sigma or pi carbon to platinum group metal bond, including

(a) 2,2'-bis(N,N-dialkylamino)1,1'-diphenyl metals, such as represented by the formula



wherein M is a platinum group metal; R_1 and R_2 are lower alkyl, e.g., from 1 to 10 carbons; and each n is, independently, an integer from 1 to 5. Representative of this group is 2,2'-bis(N,N-dimethylamino)1,1'-diphenyl palladium;

(b) tetrakis (alkoxy carbonyl) metal cycloalkenes, as represented by the formula

$$M(C_4COOR_1)_4R_2$$

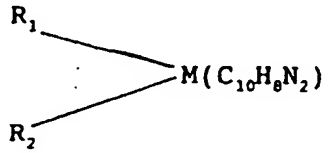
wherein M is a platinum group metal; R_1 is a lower alkyl, *e.g.*, from 1 to 5 carbons, and R_2 is a cycloalkene having, *e.g.*, from 5 to 8 carbons and from 2 to 4 unsaturations within the ring structure. Representative of this group is tetrakis (methoxy carbonyl) palladia cyclopentadiene;

(c) μ-diphenyl acetylene bis (η^5pentaphenyl cyclopentadiene) di metals as represented by the formula

$$(\Phi C\ C\Phi)\ (C_5\ M)_2$$

wherein M is a platinum group metal and Φ is phenyl. Representative of this group is μ-diphenyl acetylene bis (η^5-pentaphenyl cyclopentadiene) dipalladium;

(d) dialkyl dipyridyl metals of the formula



wherein M is a platinum group metal; and R_1 and R_2 are lower alkyl, *e.g.*, having from 1 to 5 carbons. Representative of this group is diethyl dipyridyl palladium; and

(e) bis (π-allyl) metals of the formula

$$(R\text{-}C_3H_5)_2M$$

wherein M is a platinum group metal and R is hydrogen, aryl, or alkyl, e.g., one to ten carbons. Representative of this group is bis (phenyl allyl) palladium.

Other specific suitable compounds according to the present invention include those platinum group metal-containing compositions selected from the group consisting of

f) a composition of the general formula

$$LMR^1R^2$$

wherein L^1 is either a single cyclic polyolefin or nitrogenous bidentate ligand or a pair of nitrogenous or acetylenic monodentate ligands, preferably cyclooctadienyl; M is a platinum group metal, especially platinum itself; and R^1 and R^2 are each, independently, substituted or unsubstituted lower alkyl (e.g., 1-5 carbons) benzyl, nitrobenzyl, aryl, cyclopentadiene or pentamethyl cyclopentadiene, preferably benzyl, methyl and/or phenyl;

g) a composition of the general formula

$$LMR$$

wherein L is either a single cyclic polyolefin or nitrogenous bidentate ligand or a pair of nitrogenous or acetylenic monodentate ligands; M is a platinum group metal, especially rhodium or iridium; and R is cyclopentadiene or pentamethyl cyclopentadiene;

h) a composition of the general formula

$$LM(C_4R_4)$$

wherein L is either a single cyclic polyolefin or nitrogenous bidentate ligand or a pair of nitrogenous monodentate ligands; M is platinum, palladium, rhodium, or iridium; and R is COOR, wherein R is hydrogen or alkyl having from 1 to 10 carbons, preferably methyl;

i) a composition of the general formula

$$LM(COOR)_2$$

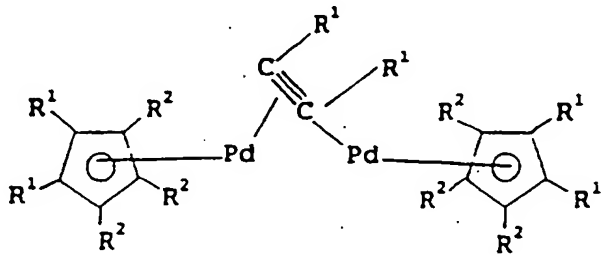
or a dimer thereof, wherein L is a non-nitrogenous cyclic polyolefin ligand, preferably cyclooctadiene or pentamethyl cyclopentadiene; M is platinum or iridium; and R is benzyl, aryl, or alkyl, preferably having 4 or more carbons, most preferably phenyl;

j) a composition comprising a reaction product of $[LRhX]_2$ and RMgX wherein L is a non-nitrogenous cyclic polyolefin ligand, preferably cyclooctadiene or pentamethyl cyclopentadiene; R is methyl, benzyl, aryl, cyclopentadiene or pentamethyl cyclopentadiene, preferably benzyl or phenyl, and X is a halide. Although presently uncharacterized, it is believed that this reaction product assumes the formula LRhR.

Functional groups which are especially preferred for use as ligands L in compositions f-j are neutral bidentate ligands such as cyclopentadiene, cyclooctadiene, pentamethyl cyclopentadiene, cyclooctatetrene, norbornadiene, o-toluidine, o-phenantholine, and bipyridine. Most preferred among monodentate ligands is pyridine.

Also useful in the present invention are

k) palladium acetylene complexes having the general formula



wherein R^1 is aryl or alkyl; and R^2 is aryl;

l) metal allyl complexes having the general formula

$$M(C_3H_5)_3 \text{ or}$$

$$M(C_3H_5\text{-}R)_2$$

wherein M is platinum group metal, especially rhodium or iridium; and R is hydrogen, aryl, or alkyl;

m) platinum (IV) compositions having the general formula

$$R_3PtR$$

wherein R is aryl, alkyl or mixtures thereof; and R is hydroxyl (-OH), acetylacetonate ($-CH_3(COCH_3)_2$), cyclopentadiene or pentamethyl cyclopentadiene (exemplary of which is trimethyl platinum hydroxide); and

n) a composition of the general formula

$$LMR$$

wherein L is substituted or unsubstituted butadiene or cyclohexadiene; M is rhodium or iridium; and R is cyclopentadiene or pentamethyl cyclopentadiene (exemplary of which are butadiene rhodium cyclopentadiene and butadi-

ene iridium cyclopentadiene.

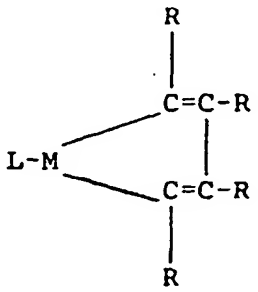
[0053] The synthesis of the preferred compounds is relatively straightforward, with the most care being taken to avoid "contamination" of the product by the objectionable functional groups discussed above. For instance, the most preferred synthetic route for production of the compounds of the formula LMR^1R^2 is by reacting commercially available platinum halides with the desired neutral ligand (except the pyridine derivative which can be added by displacement after the fact) and then reacting with a Grignard reagent having the formula R_2MgX, where X is a halide (and where the desired R^1 and R^2 in the end product are the same functional group). Where the R^1 and R^2 functional groups are desired to be different, a straightforward substitution reaction can then be run.

[0054] Exemplary of compounds suitable for use in the present invention and prepared in this manner are dipyridine platinum dibenzyl; bipyridine platinum dibenzyl; dipyridine palladium diethyl; cyclooctadiene platinum dimethyl; cyclooctadiene platinum diphenyl; cyclooctadiene platinum dibenzyl; cyclooctadiene platinum dinitrobenzyl; cyclooctadiene platinum methyl cyclopentadiene; norbornadiene platinum di-cyclopentadiene; dimethyl platinum cyclooctatetrene (which often assumes the formula dimethyl platinum cyclooctatetrene platinum dimethyl); and cyclooctadiene osmium bis (cyclopentadiene).

[0055] The compounds of the formula LMR are prepared along a similar pathway, as are the reaction products of $[LRhX]_2$ and RMgX, with the exception that the starting materials have only one R functional group and are, with respect to LMR, LRhR or LIrR. Exemplary of suitable compounds of the formula LMR are cyclooctadiene rhodium cyclopentadiene; cyclooctadiene rhodium pentamethyl cyclopentadiene; norbornadiene rhodium pentamethyl cyclopentadiene; cyclooctadiene iridium cyclopentadiene; cyclooctadiene iridium pentamethyl cyclopentadiene; norbornadiene iridium cyclopentadiene; and norbornadiene iridium pentamethyl cyclopentadiene. Exemplary of compounds which can function as the precursors for the reaction product can include cyclooctadiene rhodium chloride dimer and benzyl magnesium chloride.

[0056] Advantageously, in the Grignard-type syntheses, the Grignard reagent can be replaced by one having the formula R_2Z where Z is commonly Na, Li, K, or T1. This is especially preferred since the halides which are present in a Grignard reagent are eliminated, providing less halides in the final product and also advantageously producing a higher yield of the desired product.

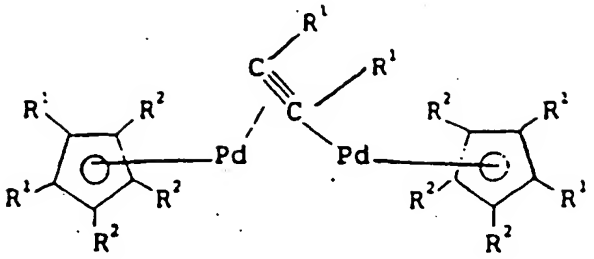
[0057] The preparation of compositions of the formula $LM(C_4R_4)$ is also straightforward and proceeds by reacting $M(dibenylidine\ acetone)_2$ with dimethylacetylene dicarboxylate in acetone and then adding the L ligand. Exemplary of suitable compounds according this formula, which has the structure



is tetrakis (methoxy carbonyl) palladia cyclopentadiene (wherein L is cyclopentadiene, M is palladium, and R is $COOH_3$).

[0058] The compositions of the formula $LM(COOR)_2$ can be prepared by reacting LMX_2, where X is a halide and a silver carboxylate such as silver benzoate. This composition can form a dimer, especially when M is platinum. Exemplary of suitable compounds having the general formula $LM(COOR)_2$ are cyclooctadiene platinum dibenzoate dimer; and pentamethyl cyclopentadiene iridium dibenzoate.

[0059] The most preferred synthetic route for production of the noted acetylene compounds is by reacting the trimeric palladium salt of a carboxylic acid ($[Pd(OOCR)_2]_3$), where R is alkyl such as methyl or ethyl, or aryl such as phenyl, like palladium acetate, propionate or benzoate, with a substituted acetylene, such as diphenylacetylene or methylphenylacetylene, in the presence of a polar solvent, such as an alcohol like methanol (CH_3OH). For example, when the reactants are palladium acetate and diphenylacetylene, the product is μ-diphenylacetylene bis(η5 pentaphenyl cyclopentadiene) dipalladium, which has the general formula



where R^1 and R^2 are each phenyl.

[0060] The disclosed metal allyl compositions can be prepared by reacting commercially available platinum group metal halides, such as $RhCl_3$ or $IrCl_3$, with an allyl Grignard reagent, such as C_3H_5MgBr, in a 3:1 molar ratio to produce the desired metal allyl, such as bis (phenyl allyl) palladium, and MgBrCl.

[0061] The platinum (IV) compositions can be prepared, for instance, by reacting $R^1{}_3PtX$, where R^1 is aryl or alkyl, such as phenyl, benzyl or methyl or mixtures and X is a halide, with NaR^2, where R^2 is cyclopentadiene or pentamethyl cyclopentadiene.

[0062] Reaction of the R_3PtX complex with aqueous acetone solutions containing a silver compound such as Ag_2O results in a product where R is hydroxyl. Alternatively, treatment of the R_3PtX complex with a solution of acetylacetone in alcoholic potassium hydroxide results in a product where R is acetyl acetonate.

[0063] The compounds of the formula LMR can be prepared by reacting commercially available metal halides with butadiene and cyclohexadienes and then reacting with a Grignard reagent having the formula RMgX, where X is a halide.

[0064] In order to provide sufficient additive, the platinum group metal compound will supply an amount of the platinum group metal within a range of at least 0.05 to 30 parts of the platinum group metal per one million parts of fuel (ppm w/v) in order to "build up" sufficient platinum group metal over time, for instance, between 50 and 1000 hours of operation. Lower times will be required where no effect on particulate trap regeneration temperature is required. Lithium or sodium compounds will aid in reducing the regeneration temperature after shorter break-in periods. A preferred range is from 0.05 to 0.5 ppm and, more preferably, the platinum group metal will be supplied at a level of from 0.10 to 0.30 ppm on the same basis.

[0065] The additive composition may include a solvent which is soluble in the fuel, such as octyl nitrate. The fuel additive compositions may also contain other additives, such as detergents, antioxidants, and cetane improvers which are known as beneficial to engine performance, but the use of such is not an essential feature of the invention.

[0066] The total amount of solvent and other additives used will depend on the dosage of platinum group metal composition required and on what is a convenient concentration to handle relative to the amount of fuel to be treated. Typically, solvent (plus other like additive) volumes of 0.1 to 40.0 liters/gram of platinum group metal com- position are acceptable.

[0067] Alternatively, the additive can be provided at a ratio so as to provide a sufficient level of platinum group metal catalyst in a relatively short period of time, *i.e.*, under about 10 hours, more preferably under about 5 hours. Effective levels to do so can range up to about 30 ppm, more advantageously, 15 to 25 ppm. These levels should be provided for 0.5 to 10 hours. Maintenance amounts of from 0.1 to 1.0 ppm can then be provided, to maintain superior activity.

[0068] In another alternative embodiment, an additive can be injected into the exhaust system, preferably just prior to the particulate trap, to supply catalyst on an initial or renewal basis. In this embodiment, the additive can contain platinum group metal and/or lithium, sodium or a combination of these. The concentration of catalyst for this use will be a level sufficient under the conditions *e.g.* from 1 to 100 ppm for the platinum group metal and from 1 to 200 ppm for the lithium or sodium. The solvent or carrier should be rapidly volatilized and any organic component of the solvent or the catalyst compounds should be capable of burning off at the steady state exhaust temperature, *e.g.* in the range of 300° to 600° C.

[0069] It has surprisingly been found that the use of the platinum group metal additives of this invention reduces the conversion of SO_2 to SO_3 as compared to conventional platinum-catalyzed particulate traps which have the platinum metal applied. This selectivity, however, does not diminish the ability of the catalyst to reduce the emissions of carbon monoxide and unburned hydrocarbons on a steady basis.

[0070] In one particularly preferred embodiment, the combination of a particulate trap and a fuel additive comprising at least a platinum group metal composition in catalytic amounts (preferably also lithium and/or sodium compositions) is employed along with a technique to control NO_x emissions, such as flue gas recirculation or retarding engine

timing. In this manner, the combined emissions of HC, CO, NO_x and particulates are reduced from what is possible with current technology.

[0071] It is an advantage of the invention that the use of the noted additives, when effective catalyst levels are built up, can reduce the ignition temperature of the particulates trapped in the particulate trap to a level whereby self-regeneration of the particulate trap, especially in a four-cycle diesel engine may occur. Even if self-regeneration cannot completely occur, *i.e.*, in a four-cycle engine which is not operating hot enough or in a two-cycle engine, the use of the described additives can reduce the temperature to which an auxiliary heat source is required to raise the diesel engine particulate trap, thereby increasing the efficiency of the use of the auxiliary heat source. In this way, further significant improvements in the use of a diesel engine particulate trap are obtained, without the art accepted tradeoff of substantially increased back pressure caused by clogging of the trap by collected particulates.

Comparative Example 1

[0072] A series of tests was carried out to determine the effect of fuel soluble platinum fuel additives on the emission of pollutants from a diesel engine operated with a particulate trap.

[0073] The engine specifications are as follows:

Engine Type	Cummins LTA10-290-B
	Engine No. 23505691
Peak Power (Measured)	230 kW at 2100 rev/min
Peak Torque (Measured)	1210 Nm at 1500 rev/min
Idle Speed	625-725 rev/min
Bore	125 mm
Stroke	136 mm
Swept Volume	10 litres
Compression Ratio	16.0:1
Fuel System	Cummins PT

[0074] The engine was installed on a standard steady state test bed and coupled to a Schenck W400 dynamometer. Gaseous and particulate emissions measurements were made 'before' and 'after' the trap by using a bypass system.

[0075] A noncatalyzed 'Corning' wall flow trap measuring 11.25" by 12" was incorporated into the engine exhaust system, which also contained a pipe with a butterfly valve bypassing the trap. This allowed the exhaust to be directed either through the trap or through the bypass pipe with the trap sealed off. In the latter case the back pressure could be adjusted by means of the butterfly valve to equal the back pressure produced by the trap.

[0076] Fuel and oil with low halide contents were employed. The fuel used was Haltermann's 0.05% Sulfur 1994 specification fuel. The fuel halide content was 3 ppm. The oil used was Amoco Premier II SAE 15W-40, analyzed as containing 27.5 ppm Chloride. The additive had the following composition and was mixed with the fuel at a dosage rate of 1:2600 by volume.

Ingredient	Parts by Weight
Diphanyl Cyclooctadiene Coordination Compound	0.0170
Ethyl D_{ii}-3 Octyl Nitrate	28.4
Ethyl EDA-2 Detergent	3.5
Xylene	2.6
Exxon LOPS Mineral Spirits	65.5

[0077] For the comparative tests without the platinum, blank additive (identical except that there is no platinum component) was mixed at the same rate. The mixed fuel was supplied to the test cell in palletted containers with a continuous recirculation system to ensure the additive stayed thoroughly mixed.

[0078] The engine test schedule was designed to provide baseline data, a period of conditioning with the additive and a repeat of tests after the conditioning:

- Phase 1 was designed to give a reliable baseline on fuel doped with blank additive; and

For Phase 2, the fuel was doped with platinum-based additive and 250 hours accumulated prior to repeating the baseline tests.

[0079] A duty cycle consisting of eight steps and six different conditions was designed to provide a mix of real-life operating conditions and to allow loading-up of the trap and regeneration. During the course of the duty cycle accumulation periods, measurements of temperatures, pressures, fuel consumption and gaseous emissions, were made at approximately ten-hourly intervals at three keypoints:

i)	Rated power	(2100 rev/min, 1065 Nm)
ii)	Peak torque	(1500 rev/min, 1210 Nm)
iii)	80% Speed, 15% load	(1680 rev/min, 177 Nm)

[0080] Five readings of fuel consumption were made to improve accuracy and allow statistical analysis of the results.

[0081] The assessment tests consisted of three four-point load range curves conducted at peak torque speed (1500 rev/min) with full measurements of emissions and particulates. Each load range curve was conducted one with exhaust flowing through the bypass and once through the trap.

[0082] Particulate papers for one pair of load range curves (through the bypass and through the trap) were analyzed for unburned oil and fuel, carbon and soluble sulfate by solid injection GC, TGA and ion chromatography respectively.

Results

Baseline Performance - With Trap

[0083] The results indicate the key features of operation of the trap.

- particulate is reduced by 85-95%
- HC is reduced
- CO is increased by up to 60% at high load

The increase in CO appears to be a result of incomplete combustion of trapped carbon and HC at regeneration conditions, as observed in other programs.

[0084] The following effects were observed after 250 hours operation on fuel doped with platinum additive:

- Little effect on Particulates and NO_x
- HC is reduced by 34-87%
- CO is reduced by 31-70%

[0085] The principal effects of using platinum additive and a trap are summarized in Figures 1-3 which show, for particulates, HC and CO, the effect of using the trap and the additive starting from baseline engine emissions normalized to 100%. These figures show two steps of emissions reduction; adding platinum additive and adding the trap.

[0086] Relative to the average baseline emissions:

- Using the platinum additive only

- Reduces HC and CO by about 35%
- Has little effect on Particulates

- Using the platinum additive in combination with a trap

  - Reduces HC and CO by about 75%
  - Reduces Particulate emissions by over 80%

Compared with other catalyst systems, the platinum additive and trap combination is able to achieve large HC and CO emissions without causing significant particulate increases from sulfate generation, even at high loads and temperatures. A possible explanation is that the platinum additive effectively creates and continually renews a very large lightly loaded catalyst in the engine, exhaust and trap. The equivalent may be difficult to achieve by conventional means due to space limitations, problems with long-term stability with very low platinum loadings, and masking of the catalyst material by carbon deposits. The addition of platinum additive will provide catalyst type benefits from reducing odor, *etc.*, without any penalties from sulphate generation.

Comparative Example 2

[0087] The additive used in combination with a trap as described above has been compared with uncatalyzed fuels, both through-flow catalysts and catalyzed trap systems.

[0088] The objective of a through-flow catalyst on diesel engines is to reduce hydrocarbon emissions without forming sulfates from the sulfur in the fuel. The benefits of through-flow catalyst are the reduction of heavy hydrocarbons (fuel and oil) in the particulate. There is also a benefit from the reduction of gaseous hydrocarbons by the reduction of odor, etc.

[0089] In order to assess catalyst systems, a comparison is made between the conversion efficiency for gaseous hydrocarbons and the conversion efficiency for sulfur in the fuel that occurs in the catalysts over a range of conditions. In Figures 4 and 5 results are shown for HC and fuel sulfur conversion efficiency for the platinum additive and trap as tested in Example 1 and three catalysts on the exhaust of uncatalyzed diesel fuel. Catalyst A was an active catalyst with high conversion efficiency and catalysts B and C were more selective formulations which have suppressed sulfur conversion at the expense of some loss of HC conversion. The horizontal exis in the figures is the inlet temperature to the catalyst.

[0090] The HC conversion efficiency (Figure 4) for the platinum additive and trap combination is as high as the most active catalyst A but the sulfur conversion efficiency (Figure 5) is much lower and stays below 1% up to 670°C. This is further illustrated by Figure 6 which shows the same data as a trade-off between sulfur and HC conversion. In this figure the optimum is to have a system which operates in the bottom right hand corner, maximizing HC conversion with little sulfur conversion (sulfate generation) penalty on particulates. The platinum additive and trap combination is clearly excellent in this respect.

Claims

1. A method for improving the operation of a diesel engine equipped with a diesel trap, comprising:

   adding to a diesel fuel, a platinum group metal composition in an amount of at least 0.05 ppm up to 30 ppm and at least one of a cerium compound, an iron compound and a copper compound in an amount of from 5 to 100 ppm, the amounts being effective to lower the emissions of unburned hydrocarbons and carbon monoxide and to lower the temperature at which particulates are burned from the trap; operating the diesel engine by burning the fuel over a sufficient period of time to produce exhaust gases and achieve a sustained reduction in unburned hydrocarbons and carbon monoxide; and

   passing the exhaust gases from the operation of the engine through the diesel trap whereby particulates are collected in the trap and burned therein at a temperature lower than could be achieved in the absence of the platinum group metal and the cerium, iron or copper.

2. A method of claim 1 wherein said diesel engine is modified by retarding engine timing effectively to reduce NOx emissions.

3. A method of claim 1 wherein said diesel engine is modified by recirculating exhaust gas effectively to reduce NOx emissions.

4. A method of claim 1 wherein a cerium compound is added to said fuel.

5. A method of claim 1 wherein a copper compound is added to said fuel.

6. A method of claim 1 wherein an iron compound is added to said fuel.

Patentansprüche

1. Verfahren zum Verbessern des Betriebes eines Dieselmotors, der mit einem Dieselpartikelfilter ausgerüstet ist, umfassend:

   Zusetzen einer Zusammensetzung mit einem Metall der Platingruppe in einer Menge von mindestens 0,05 ppm bis zu 30 ppm und mindestens einer Verbindung aus Cerverbindung, Eisenverbindung und Kupferverbindung in einer Menge von 5 bis 100 ppm zu einem Dieselkraftstoff, wobei die Mengen eine Verringerung der Emissionen an unverbrannten Kohlenwasserstoffen und Kohlenmonoxid und ein Absenken der Temperatur bewirken, bei der Feststoffteilchen aus dem Filter verbrannt werden; Betreiben des Dieselmotors durch Verbrennen des Kraftstoffes über einen ausreichenden Zeitraum, um Abgase zu erzeugen und eine anhaltende Verminderung an unverbrannten Kohlenwasserstoffen und Kohlenmonoxid zu erreichen; und
   Durchleiten der Abgase aus dem Betrieb des Motors durch den Dieselpartikelfilter, wodurch Feststoffteilchen in dem Filter gesammelt und darin bei einer Temperatur verbrannt werden, die niedriger ist als die, die in Abwesenheit des Metalls der Platingruppe und des Cers, Eisens oder Kupfers erreicht werden könnte.

2. Verfahren nach Anspruch 1, wobei der genannte Dieselmotor dadurch abgeändert wird, daß die Motorzeitsteuerung effektiv verzögert wird, um NOx-Emissionen zu vermindern.

3. Verfahren nach Anspruch 1, wobei der genannte Dieselmotor dadurch abgeändert wird, daß das Abgas effektiv zurückgeführt wird, um NOx-Emissionen zu vermindern.

4. Verfahren nach Anspruch 1, wobei dem genannten Kraftstoff eine Cerverbindung zugesetzt wird.

5. Verfahren nach Anspruch 1, wobei dem genannten Kraftstoff eine Kupferverbindung zugesetzt wird.

6. Verfahren nach Anspruch 1, wobei dem genannten Kraftstoff eine Eisenverbindung zugesetzt wird.

Revendications

1. Procédé pour améliorer le fonctionnement d'un moteur diesel pourvu d'un piège diesel, comprenant :

   l'ajout au combustible diesel d'une composition d'un métal du groupe du platine suivant une quantité d'au moins 0,05 ppm jusqu'à 30 ppm et d'au moins l'un des composé de cérium, un composé de fer et un composé de cuivre suivant une quantité de 5 à 100 ppm, les quantités étant efficaces pour diminuer les émissions d'hydrocarbures non brûlés et de monoxyde de carbone et pour diminuer la température à laquelle les particules sont brûlées à partir du piège ; le fonctionnement du moteur diesel par brûlage du combustible pendant une période de temps suffisante pour produire des gaz d'échappement et arriver à une réduction prolongée en hydrocarbures non brûlés et en monoxyde de carbone ; et le passage des gaz d'échappement du moteur en fonctionnement à travers le piège diesel, de façon que les particules soient recueillies dans le piège et y soient brûlées à une température inférieure à celle qui serait atteinte en l'absence d'un métal du groupe du platine et de cérium, fer ou cuivre.

2. Procédé selon la revendication 1, dans lequel ledit moteur diesel est modifié en retardant le temps du moteur effectivement pour réduire les émissions de NOx.

3. Procédé selon la revendication 1, dans lequel ledit moteur diesel est modifié en recyclant le gaz d'échappement effectivement pour réduire les émissions de NOx.

4. Procédé selon la revendication 1, dans lequel un composé de cérium est ajouté audit combustible.

5. Procédé selon la revendication 1, dans lequel un composé de cuivre est ajouté audit combustible.

6. Procédé selon la revendication 1, dans lequel un composé de fer est ajouté audit combustible.

Fig. 1

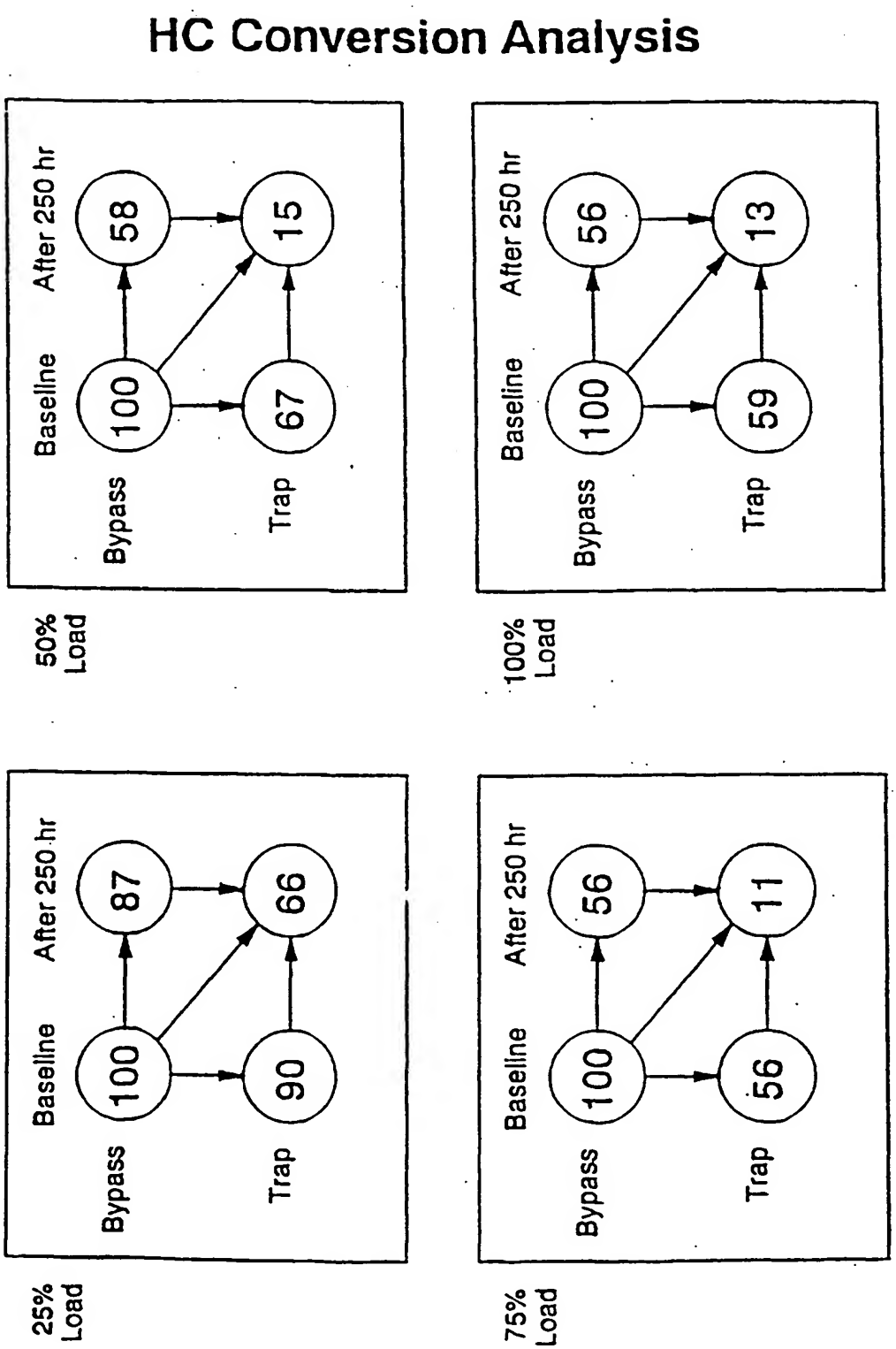

HC Conversion Analysis
50% Load
Baseline
After 250 hr
Bypass
Trap
100
58
67
15
100% Load
100
56
59
13
25% Load
100
87
90
66
75% Load
100
56
56
11

FIG. 12

CO Conversion Analysis

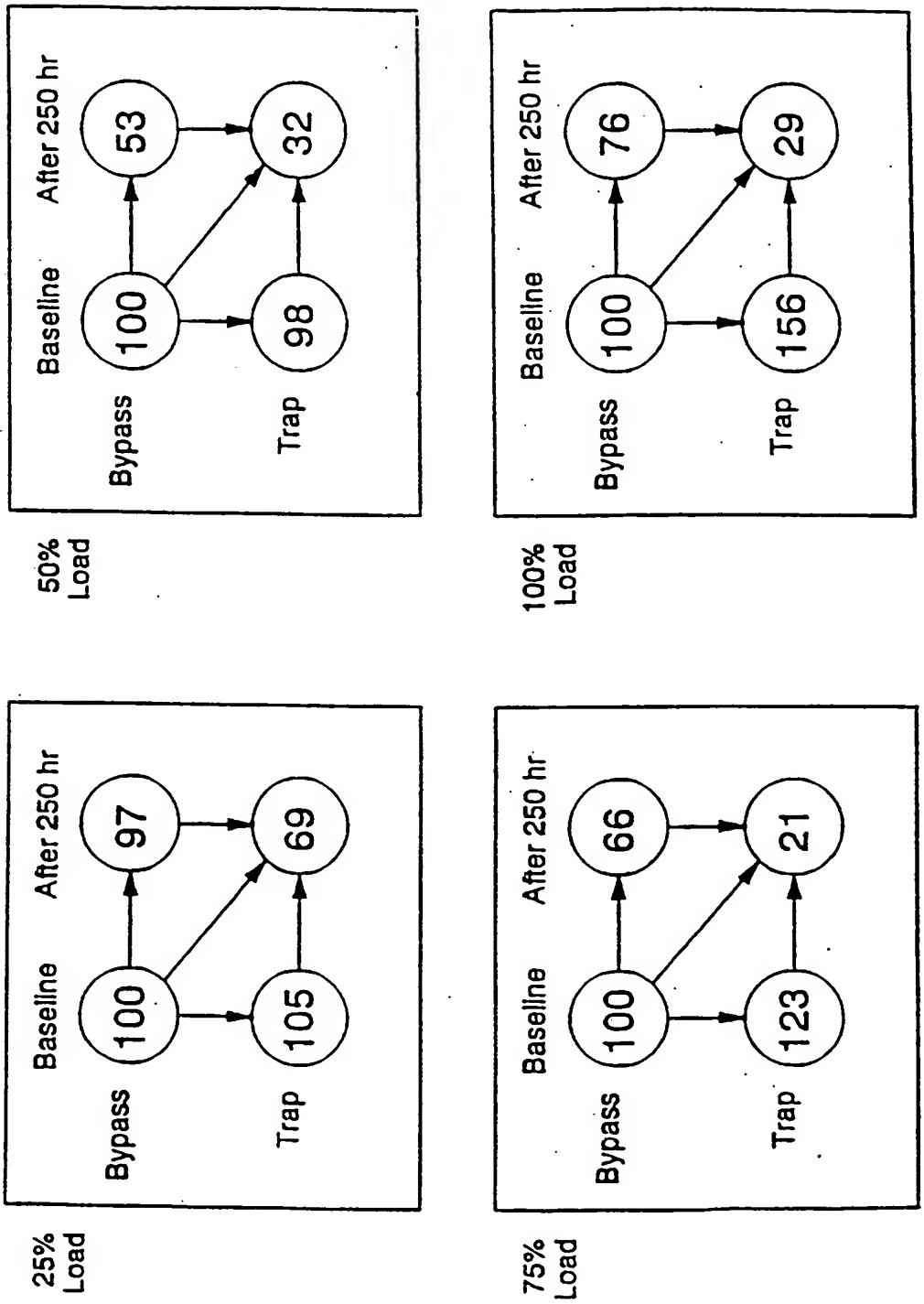


FIG. 3

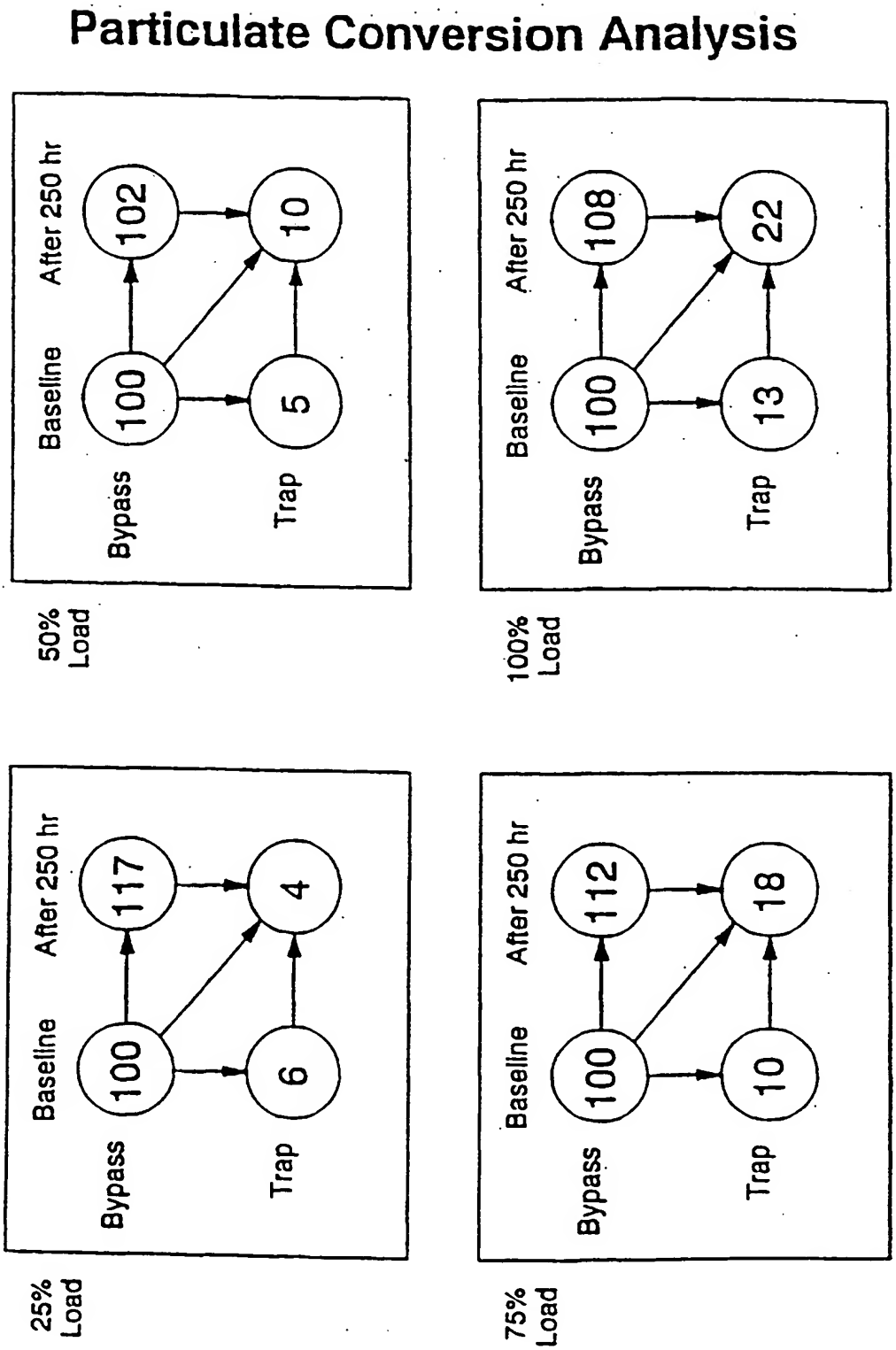

Particulate Conversion Analysis
50% Load
Baseline
After 250 hr
Bypass
100
102
Trap
5
10
100% Load
Baseline
After 250 hr
Bypass
100
108
Trap
13
22
25% Load
Baseline
After 250 hr
Bypass
100
117
Trap
6
4
75% Load
Baseline
After 250 hr
Bypass
100
112
Trap
10
18

Fig. 4

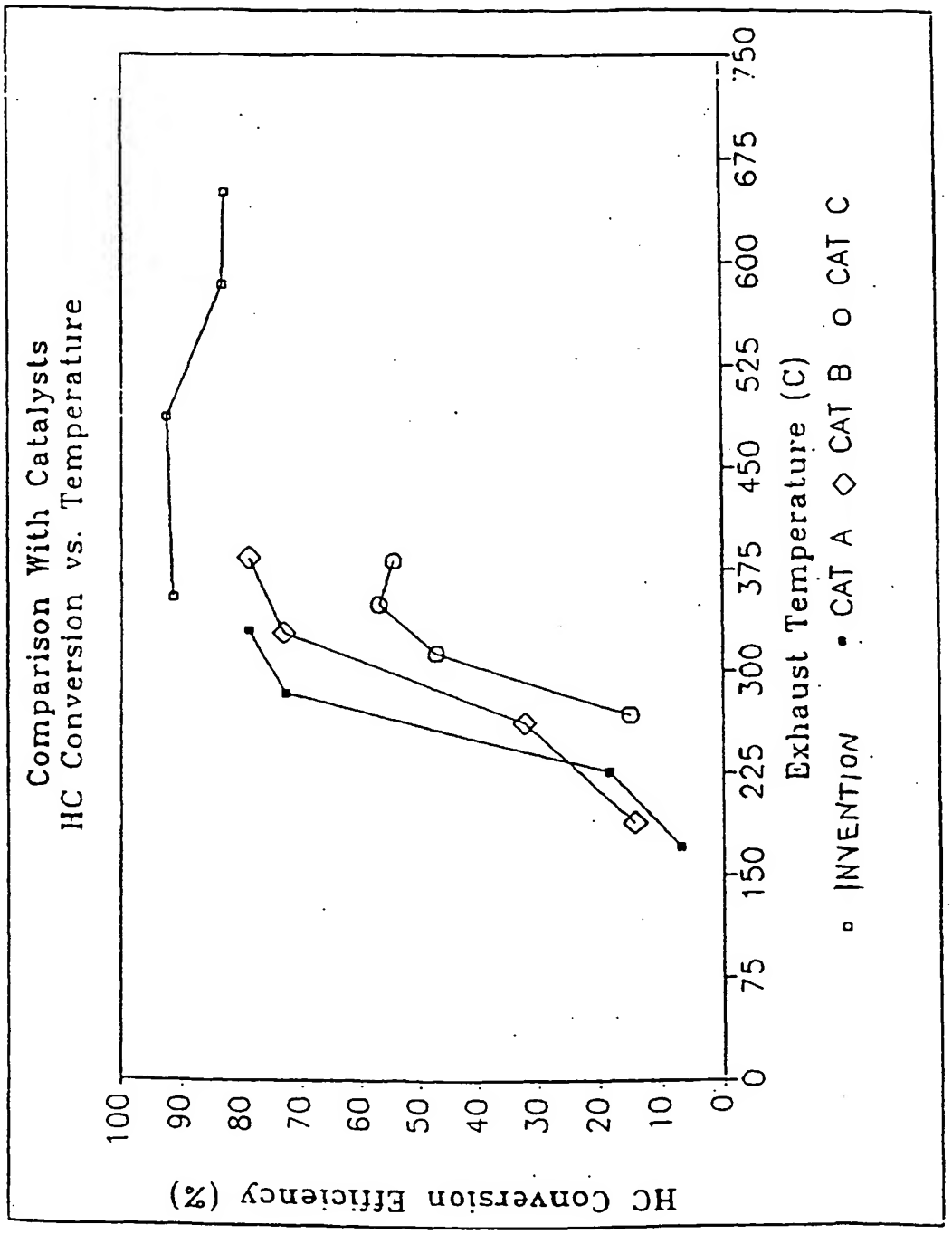

Comparison With Catalysts
HC Conversion vs. Temperature
HC Conversion Efficiency (%)
100
90
80
70
60
50
40
30
20
10
0
0
75
150
225
300
375
450
525
600
675
750
Exhaust Temperature (C)
▫ INVENTION
▪ CAT A
◇ CAT B
○ CAT C

FIG. 5

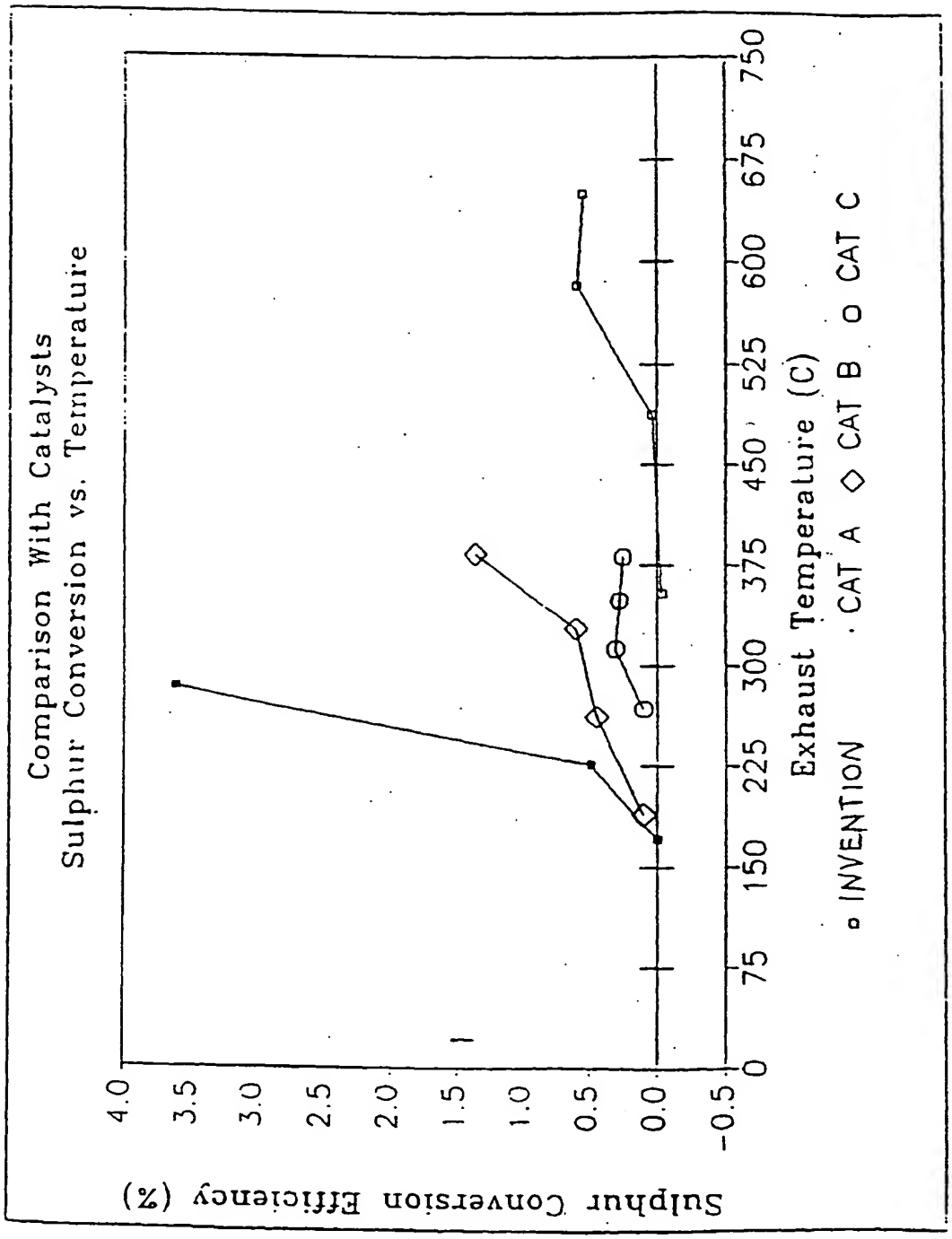
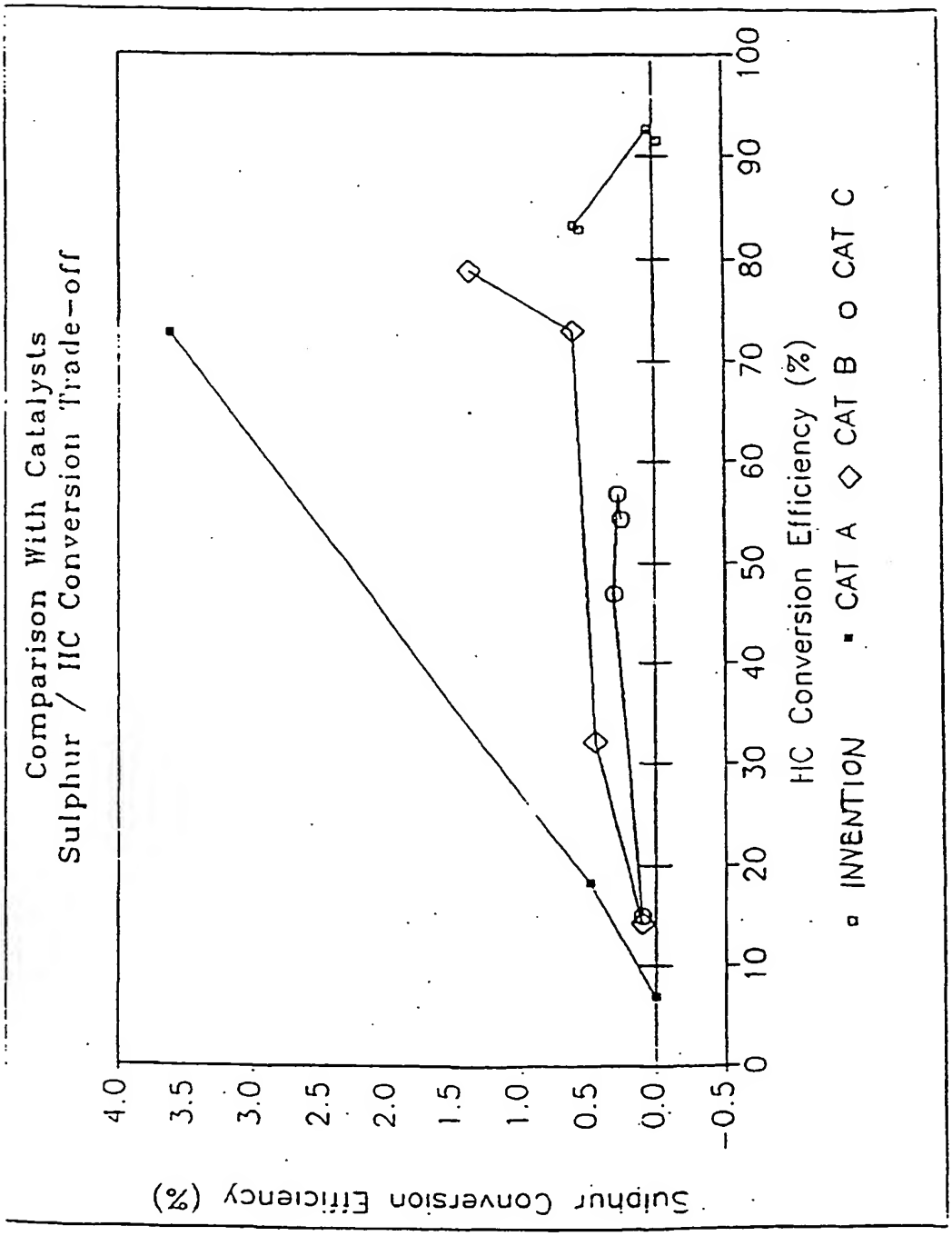

Comparison With Catalysts
Sulphur Conversion vs. Temperature
Sulphur Conversion Efficiency (%)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0
75
150
225
300
375
450
525
600
675
750
Exhaust Temperature (C)
▫ INVENTION
· CAT A
◇ CAT B
○ CAT C

FIG. 6


Comparison With Catalysts
Sulphur / HC Conversion Trade-off
Sulphur Conversion Efficiency (%)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0
10
20
30
40
50
60
70
80
90
100
HC Conversion Efficiency (%)
▫ INVENTION ▪ CAT A ◇ CAT B ○ CAT C